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AMERICAN UNIV WASHINGTON DC DEPT OF CHEMISTRY
LOCALIZED ELECTROCHEMICAL CORROSION CELLS.(U)
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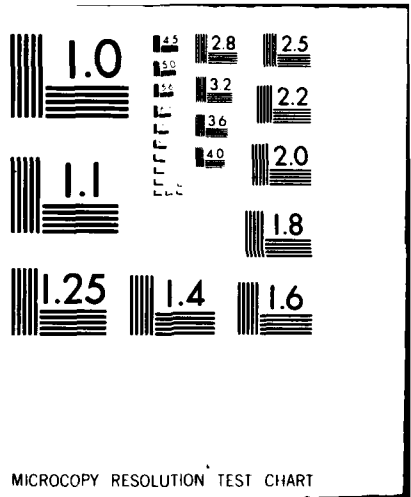
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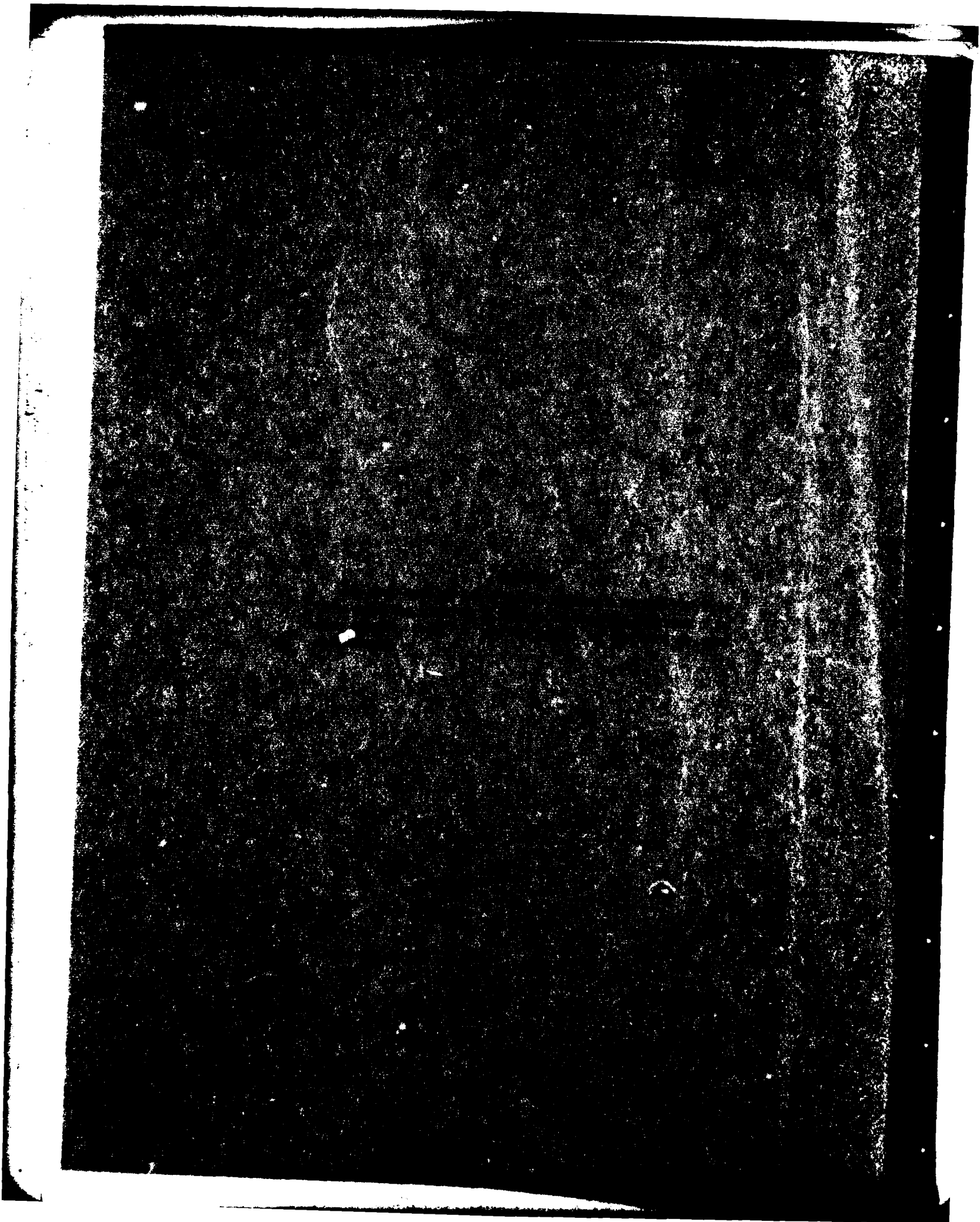
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Localized Electrochemical Corrosion Cells		5. TYPE OF REPORT & PERIOD COVERED Final Report 09/01/78 - 2/28/82
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Foley, R.T.		8. CONTRACT OR GRANT NUMBER(s) DAAG29-78-G-0165 DAAG29-80-C-0148
9. PERFORMING ORGANIZATION NAME AND ADDRESS The American University Washington, D.C. 20016		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Research Office P.O. Box 12211 Research Triangle, NC 27709		12. REPORT DATE February 1982
		13. NUMBER OF PAGES 12 + i
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, Distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Corrosion, stress cracking, aluminum alloys, localized corrosion complex ions.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this research has been to characterize the chemical and electrochemical nature of the localized corrosion cell on aluminum alloys and to relate the environment to the rate of stress cracking of AA7075.		

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AR(3+) → It was demonstrated that the environment, as represented by various anions in solution enters into the stress cracking process in a specific way. The reaction at the crack tip is chemical in nature. There are significant changes in pH and Al+++ concentration within the crack. These changes have been measured and are dependent on the anion in solution as well as the applied potential. The environment within the crack may be altered as well as concentrated, e.g. nitrate ion may be reduced to ammonia during the cracking process. The low pH - of approximately 3 - is explained by the hydrolysis of the aluminum ion, but it is not the hydrolysis, per se, that is responsible for the accelerated corrosion, because the corrosion rate of aluminum in different aluminum salts at the same pH is significantly different.

All of the studies taken together convincingly demonstrate that chemical reactions at the crack tip determine the rate of crack growth in AA7075. Moreover, these chemical reactions are usually specifically dependent on the environment, the anion in solution, because the anion in turn dictates the nature (stability or instability) of the aluminum - anion complexes formed at the reaction site.

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"LOCALIZED ELECTROCHEMICAL CORROSION CELLS"

FINAL REPORT

Covering period from September 1,
1978 through February 28, 1982

by R.T. Foley

February 1982

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park
North Carolina 27709
DAAG29 - 78 - G - 0165
DAAG29 - 80 - C - 0148

The American University
Washington, D.C. 20016

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STATEMENT OF THE PROBLEM

The most serious types of corrosion, from an engineering standpoint, are localized in nature. These include pitting, crevice corrosion, stress corrosion cracking, and probably fatigue corrosion. The distinguishing feature of localized corrosion, as contrasted to general corrosion, is that the chemical environment in the local cell differs significantly from that in the general environment. Usually the solution in the local cell is more concentrated, both in hydrogen ions and in electrolyte, but there has not been done sufficient work to describe the expected difference in a quantitative manner.

The objective of this research has been to characterize the chemical and electrochemical nature of the localized corrosion cell on aluminum alloys and to relate the environment to the rate of stress cracking of AA 7075.

It should follow that, with a good description of the localized cell, the design of preventive or counter measures against stress corrosion cracking of high strength aluminum alloys will be possible.

SUMMARY OF THE MOST IMPORTANT RESULTS

The findings of this investigation demonstrated clearly that the environment, as represented by various electrolytes, enters into the stress corrosion process in a specific manner (1). First, it should be said that water, in the vapor state or condensed state, is a sufficient agent for stress cracking. However, in a given electrolyte the effect of anions generally over-rides that of water and, in certain solutions, can nullify the effect of water. For example, AA 7075 - T651 will crack in the vapor over sodium sulfate solution, but crack growth will be inhibited if the test sample is immersed in the solution.

By comparing the results of this investigation and previous investigations in our laboratory, it is possible to make

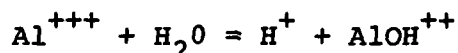
(1) The number in the parenthesis refers to the Publication listed below. The ABSTRACT of the corresponding publication can be found in the APPENDIX of the report.

a qualitative correlation between the ability of a specific anion to activate the aluminum surface to initiate pitting and general corrosion, in the first case, and to promote crack growth in the second. This behavior, of course, indicates that a key step in stress corrosion cracking is a chemical one. In this study many anions were investigated, and, generally speaking, the crack growth can be explained in terms of the ability of the anion to activate the aluminum surface. For example, oxalic and tartaric acids form soluble, stable, complex ions with aluminum, and cracking proceeds rapidly in the presence of these acids. Chloride also forms soluble, transitory, complexes, but sulfate forms stable, coordination compounds.

It is well documented that the electrolyte concentration within a crack or crevice is substantially different from that in the bulk solution. However, it is also now apparent that the corrodent in the crack may itself be altered during the stress cracking process (2). The high oxidation potential of the bare, oxide-free, aluminum at the tip of the crack may reduce specific anion species. This effect has been demonstrated with nitrate ion, which is usually an inhibitor, but it should also apply to other oxyanions. The effect can be illustrated by comparing the crack growth behavior in chloride and nitrate solutions. In chloride solution, at open circuit potential and when polarized anodically, the crack tip is acid and crack growth proceeds; when polarized to a potential of -1.3V (vs SCE) no cracking is observed. In nitrate solution, when polarized anodically, no stress cracking occurs. At open circuit potential and when polarized cathodically, nitrate is reduced to ammonia, the crack tip becomes basic and stress cracking proceeds rapidly.

It is generally recognized that the pH of the solution in a growing pit on an aluminum alloy, or, in a crack in a stress-cracking specimen of an aluminum alloy, is approximately 3.5, and there appears to be a relatively high concentration of Al^{+++} . The question arises whether the enhanced local corrosion is due

to the low pH produced by the hydrolysis of the aluminum ion or to the specific salt (arising from a specific anion) (3). Salts such as aluminum nitrate, bromide, chloride, sulfate, perchlorate, and iodide all hydrolyze to give solutions in a narrow pH range of 3.0 ± 0.5 . In this pH range, the hydrolysis of the aluminum ion can be represented by



In spite of the narrow pH range of the solutions produced by hydrolysis, the corrosion rates of alloys 1199 and 7075 are significantly different in these different salt solutions. Aluminum nitrate and iodide are very aggressive. The corrosion rate in aluminum sulfate solution is appreciably less than the rate in aluminum bromide, aluminum chloride, or aluminum perchlorate. These experiments established the point that it is not the hydrolysis, per se, that is, the generation of the hydrogen ion, that determines the rate of localized corrosion, but rather the specific salt in the solution.

Having established the fact that the dissolution rates of AA 1199 and AA 7075 were significantly different in various aluminum salt solutions, the reason for these differences was sought. The possibility that these differences in corrosivity were based on differences in structure at the molecular level was investigated by examining the infrared spectra of these salt solutions (4). All of these electrolytes did effect the structure of water, but only in the case of aluminum nitrate was there evidence for cation-anion interaction. A new absorption band (not reported in the literature) indicated that dimerization was occurring at a pH lower than reported in the literature. The results from these infrared studies led to the conclusion that differences in structure did not lie in the formation of new bonds, such as Al-O-Cl, but must occur at the macro level, eg. ionic complexes.

The principal objective of this investigation was to achieve a better description of the composition of the solution inside the stress crack, or, a better understanding of the nature of the "occluded" cell (5). To this end, the composition of the solutions inside the advancing cracks of stress corroding specimens was analyzed semi-quantitatively. Also, the relationship between composition and applied potential was investigated along with the morphology of the stress corrosion crack wall under different conditions.

The effect of potential is dependent on the specific anion in solution. Thus, in NaCl solution, crack growth ceases when polarized cathodically to -1.06 V (vs SHE), (arguing against a hydrogen mechanism in this electrolyte). In Na_2SO_4 solution, crack growth is slow at open circuit potential but polarizing to -1.186 V causes the crack to propagate at an appreciable rate. In NaNO_3 solution, the crack growth accelerates at potentials negative to the open circuit potential as discussed above under alteration of corrodent.

The chemical composition of the solution within the crack proper, i.e. the H^+ and Al^{+++} concentrations, are determined in part by the applied potential. In NaCl solution, the pH goes from 3.4 to 1.8 on polarizing anodically from the open circuit potential; the Al^{+++} concentration in the growing crack at open circuit potential is 0.25 M and goes to 0.4 M at a positive potential. Polarizing cathodically moves the pH to 12 and reduces the soluble Al^{+++} to 0.01 M. Results which were similar qualitatively were obtained in Na_2SO_4 solution. However, the pH of the solution in the crack grown in NaNO_3 solution is 7.3 under anodic polarization and 12.5 under cathodic polarization. In the cathodically polarized sample, the Al^{+++} concentration is 0.2 M as compared with 0.05 M in the crack formed when stress corrosion cracking occurs at open circuit potential.

These analytical measurements were made with a freezing technique, a technique adopted after considering several other procedures. In this technique, the sample is removed from the test solution after the crack had progressed a reasonable dis-

tance, and immersed in an acetone-dry ice mixture. The frozen test specimen is split open, and as the solution thaws, is analyzed in situ. The pH is determined with "Pehanon" pH indicator papers, with a precision of 0.2 pH units. The Al^{+++} is determined with filter papers impregnated with morin and quinalizarin solutions which are aluminum ion sensitive reagents. Where several drops of a solution are available, for example, in a simulated crevice, the Al^{+++} determination is made spectrophotometrically with Eriochrome Cyanine-R reagent.

The scanning electron microscope examination of the cracks after removal from the test solution revealed that normally the crack geometry followed what would be expected in an "occluded" cell. The tip of the crack which was the anode was bright and shiny and free of any film, the cathode was covered with aluminum hydroxide, and a typical reaction product pattern was intermediate.

All of these studies taken together convincingly demonstrate that chemical reactions at the crack tip determine the rate of crack growth in AA 7075. Moreover, these chemical reactions are usually specific, dependent entirely on the environment, the anion in solution, because the anion in turn dictates the nature (stability or instability) of the aluminum anion complexes formed at the reaction site.

PUBLICATIONS

- (1) "The Chemical Nature of Aluminum Corrosion: IV. Some Anion Effects on SCC of AA 7075 - T651", Ahn H. Le, B. F. Brown, and R. T. Foley, CORROSION, 36, 673-679 (1980).
- (2) "Alteration of Corrodent Ion Species Within Stress Corrosion Cracks", Trung H. Nguyen, B. F. Brown, and R. T. Foley, J. Electrochemical Society, accepted for publication.
- (3) "The Chemical Nature of Aluminum Corrosion: I Corrosion of Aluminum Surfaces by Aluminum Salts", K. Sodoudeh, T. H. Nguyen, R. T. Foley, CORROSION, 37, 358-362 (1981).
- (4) "Infrared Spectra of Aluminum Salt Solutions", J. F. McIntyre, R. T. Foley, and B. F. Brown, Applied Spectroscopy, Volume 36, Number 2, (1982).
- (5) "On the Nature of the Occluded Cell in Stress Corrosion Cracking - Effect of Potential, Composition, Morphology", T. H. Nguyen, B. F. Brown, and R. T. Foley, CORROSION, submitted for publication.

PARTICIPATING SCIENTIFIC PERSONNEL

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Dr. R. T. Foley, Co-principal Investigator

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APPENDIXES

(1) THE CHEMICAL NATURE OF ALUMINUM CORROSION: IV. SOME ANION EFFECTS ON SCC OF AA 7075-T651*

Anh H. Le, B. F. Brown, and R. T. Foley

ABSTRACT

Double bolt loaded double cantilever beam specimens were used. Increasing chloride ion concentration increased the stress corrosion cracking (SCC) plateau growth rate up to about 0.6 M, presumably by increasing the activation of the aluminum surface; at high concentrations the cracking was slower, perhaps because of lower solubility of oxygen. No analyses or potential measurements were made inside the crack, but nominal external potential and pH values especially for benzoate and ammonium hydroxide indicated that a large potential drop must be obtained within the crack if a hydrogen mechanism is involved, at least in those solutions. The activity of water in aqueous solutions of various salts did not correlate with the SCC rates, indicating that specific ion effects dominated. The nitrate ion is reduced by 7075 to ammonia, though this is slow in concentrated nitrate solution; perchlorate ion was not observed to be reduced to soluble chloride. In general, the substances which activate the aluminum surface as by forming soluble complex ions with aluminum caused rapid cracking, though there were exceptions such as benzoate, which inhibited corrosion but promoted SCC. The rate of SCC in various commercial plates of 7075 was similar in some environments, but very different from plate to plate in other environments.

*(reprinted from CORROSION, 36, 673-679 (1980))

(2) ALTERATION OF CORRODENT ION SPECIES
WITHIN STRESS CORROSION CRACKS*

Trung H. Nguyen, B. F. Brown, and R. T. Foley

ABSTRACT

The composition of the solution within the stress corrosion crack may be altered during the cracking process. The bare, oxide-free, aluminum reduces nitrate to ammonia. Potential has an influence also as seen by the following comparison between chloride and nitrate.

Potential	NaCl	NaNO ₃
Open circuit potential	Acid crack tip, SCC	Basic crack tip, NH ₃ , SCC
Polarized anodically	Acid crack tip, SCC	Near neutral crack tip, no NH ₃ detected, no SCC
Polarized cathodically (-1.3 V vs SCE)	Basic crack tip, no SCC	Basic crack tip, much NH ₃ , SCC

*(J. of the Electrochemical Society, accepted for publication)

(3) THE CHEMICAL NATURE OF ALUMINUM
CORROSION: I CORROSION OF ALUMINUM
SURFACES BY ALUMINUM SALTS*

K. Sotoudeh, T. H. Nguyen, R. T. Foley, and B. F. Brown

ABSTRACT

The corrosion of aluminum (alloys 1199-H14 and 7075-T651) by solutions of $\text{Al}(\text{NO}_3)_3$, AlBr_3 , AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}(\text{ClO}_4)_3$, AlI_3 , and NaCl of various concentrations has been measured. Experiments were also conducted in saturated solutions of aluminum acetate, benzoate, phosphate, chromate, and fluoride. The dissolution rate of the alloys varies considerably with the salt, the nitrate and iodide being most aggressive. The corrosion rate in sulfate solutions is much less than the rate in bromide, chloride, or perchlorate. The pH of the various salt solutions is not the determining parameter, but for a given salt (AlCl_3) the corrosion rate increases with the decrease in pH. The hydrolysis of the salts was considered from the viewpoint of assessing the significance of the hydrolysis reaction on aluminum corrosion. Salts such as AlCl_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$, and AlBr_3 are treated as the salts of the respective strong acid and the weak base $\text{Al}(\text{OH})^{++}$ with a pK_b of 8.67. The conjugate acid of this weak base is the hydrated aluminum ion. An attempt to correlate the hydrolysis, i.e., generation of hydrogen ion, with the ability of the salt to corrode aluminum (1199 and 7075) leads to the conclusion that it is not the hydrolysis, per se, that is the governing factor but rather the other chemical species in solution.

*(reprinted from CORROSION, 37, 358-362 (1981))

(4) INFRARED SPECTRA OF ALUMINUM SALT SOLUTIONS*

J. F. McIntyre, R. T. Foley, and B. F. Brown

ABSTRACT

Aluminum salt solutions activate metallic aluminum surfaces at different rates. The objective of this investigation was to attempt to establish whether or not structural differences at the molecular level could account for the chemical reactivity. The infrared spectra of various concentrations of aluminum chloride, aluminum nitrate, aluminum perchlorate, and aluminum sulfate were measured. The spectra included several general features (1) a broadening of the OH stretching band of water, (2) a splitting of the OH stretch of water into several absorption bands, (3) the emergence of a new absorption band at 2400 cm^{-1} (related to dimer formation), (4) splitting of the NO_3^- absorption band at 1370 cm^{-1} , (5) occasional splitting of the OH bending mode of water, (6) no direct evidence of anion-cation interaction for AlCl_3 , $\text{Al}(\text{ClO}_4)_3$, and $\text{Al}_2(\text{SO}_4)_3$. In general, there was no difference at the molecular level between these aluminum salt solutions that would account for differences in chemical reactivity.

*(Applied Spectroscopy, volume 36, number 2 (1982))

(5) "ON THE NATURE OF THE OCCLUDED CELL IN
STRESS CORROSION CRACKING - EFFECT OF POTENTIAL,
COMPOSITION, MORPHOLOGY"*

T. H. Nguyen, B. F. Brown, and R. T. Foley

ABSTRACT

The SCC of Al alloy 7075 has been investigated in various salt solutions and at different applied potentials. In sodium chloride solution, the pH at the crack tip is acidic at the open circuit and in the anodic potential range while, in the cathodic range, it is basic. At the critical cathodic potential of -1.056 V. vs SHE, crack growth is at its minimum. In Na_2SO_4 solution, crack propagation is very slow at the open circuit and at anodic potentials even though the pH at the crack tip is acidic. However, when the potential is shifted to a cathodic range, the crack begins to propagate at an appreciable rate. In NaNO_3 solutions, crack propagation rate increases in the cathodic range with formation of ammonia. No crack growth was observed in the anodic range. Using a crevice corrosion set-up, it is found that the solutions existing inside a crevice and a crack are very similar.

The morphology of the crack wall surfaces in these solutions has been observed with the scanning electron microscope, and a mechanism for the crack propagation has been proposed.

*(CORROSION, Submitted for Publication)